

PCT/IL 00 / 00 588

10/089050



1600/588

מדינת ישראל
STATE OF ISRAEL

REC'D 24 NOV 2000	
WIPO	PCT

Ministry of Justice
Patent Office

משרד המשפטים
לשכת הפטנטים

REC'D 24 NOV 2000	
WIPO	PCT

This is to certify that
annexed hereto is a true
copy of the documents as
originally deposited with
the patent application
of which particulars are
specified on the first page
of the annex.

זאת לתעודה כי
רצופים בזה העתקים
נכונים של המסמכים
שהופקדו לכתילה
עם הבקשה לפטנט
לפי הפרטים הרשומים
בעמוד הראשון של
הנספח.

**PRIORITY
DOCUMENT**
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

This 26 -09- 2000 היום

רשם הפטנטים

Commissioner of Patents

נתאשר
Certified

לשימוש הלשכה
For Office Use

חוק הפטנטים, התשכ"ז-1967
PATENTS LAW, 5727-1967

ב ק ש ה ל פ ט נ ט

Application for Patent

132022	מספר: Number
23-09-1999	תאריך: Date
	הוקדם/נרחה Ante/Post-dated

אני, (שם המבקש, מענו - ולגבי גוף מאוגד - מקום התאגדותו)
I (Name and address of applicant, and, in case of a body corporate, place of incorporation)

פרופ' סטוארט ליכט, רחוב סורוקה מספר 39, חיפה 34759.

Prof. Stuart LICHT, of 39, Soroca St. Haifa 34759.

בעל אמצאה מכח הדין ששמה הוא:
Owner, by virtue of by law of an invention, the title of which is:

ייצור אלקטרוליטי של מלחי ברזל (שש ערכי)

(בעברית)
(Hebrew)

ELECTROLYTIC PRODUCTION OF SOLID Fe(VI) SALTS

(באנגלית)
(English)

המבקש בואת כי ינתן לי עליה פטנט.
hereby apply for a patent to be granted to me in respect thereof.

* בקשת חלוקה - Application for Division		* בקשת פטנט מוסף - Application for Patent of Addition			* דרישת דין קדימה Priority Claim	
מבקשת פטנט from Application		* לבקשה/לפטנט to Patent/Appl.		מספר/סימן Number/Mark	תאריך Date	מדינת האיגוד Convention Country
No. _____ מס' _____ dated _____ מיום _____		No. _____ מס' _____ dated _____ מיום _____				
* יפוי כח: כללי/ספציפי / עור יוגש P.O.A.: general / specific - attached / to be filed later - הוגש בענין _____ Has been filed in case _____						
המען למסירת הודעות ומסמכים בישראל Address for Service in Israel שמעון לביא, עורר-פטנטים (99171) ת.ד. 6202, חיפה 31060 Simon Lavie, P.O. Box 6202, Haifa 31060						
חתימת המבקש Signature of Applicant		היום 22 בחודש ספטמבר שנת 1999 This of 1999				
Simon Lavie		לשימוש הלשכה For Office Use				

**"ELECTROLYTIC PRODUCTION OF SOLID
Fe (VI) SALTS"**

"ייצור אלקטרוליטי של מלחי ברזל (שש ערכי)"

ELECTROLYTIC PRODUCTION OF SOLID Fe(VI) SALTS

The present invention relates to the novel preparation of Fe(VI) salts. More particularly the invention relates to a method for the preparation of Fe(VI) salts, also known as Super-iron or ferrates, based on direct electrolytic synthesis into the solid-phase.

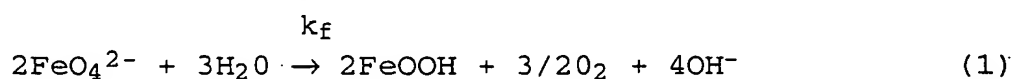
BACKGROUND OF THE INVENTION

There is an ongoing need for providing chemical oxidizing agents which are low-cost and are acceptable by the environment for a wide variety of applications including improved batteries, chemical synthesis and water purification. For example, for batteries, *prima facie*, salts containing iron in the +6 valence state, hereafter called Fe(VI) which are capable of multiple electron reduction, would be capable to provide a higher cathode storage capacity.

Fe(VI) salts such as sodium, potassium and calcium/sodium ferrates, have been previously electrochemically formed by anodic dissolution which forms a solution containing dissolved Fe(VI). This has been reported by J. P. Deininger et al. (U.S. Patents 4451338, 4435257 and 435256), and more recently by Devir et al. (J. App. Electrochem. 26, 823-827, 1996) and by Bouzek et al (Electrochem. Commun. 1, 370-374, 1999). Following this, solid Fe(VI) salts may be recovered by precipitation as a solid adduct.

Electrochemical synthesis by anodic dissolution has several unattractive features. These include that Fe(VI) is produced only in a highly dilute, and hence less useful, form. Typically

Fe(VI) is synthesized by anodic dissolution only up to approximately 1% by weight, or less, of the solution. Another unattractive feature of anodic dissolution synthesis is the need for additional materials to recover by precipitation the solid Fe(VI) adduct. Still another unattractive feature of anodic dissolution synthesis is the loss of Fe(VI) during synthesis due to decomposition. This iron decomposition to a less oxidized form (i.e. to a lower valence state) can occur very rapidly. The stability of Fe(VI) salts solutions often being only on the order of a few hours at room temperature. (Anal. Chem. 23, 1312-4, 1951). Later, in a report by H. Goff et al (J. Amer. Chem. Soc. 93, 6058-6065, 1971) it was mentioned that only little is known on the chemistry of Fe(VI) salts. The decomposition of iron to a lower valence, loses spontaneously the oxidative feature of the Fe(VI) salt. In its reaction with water the Fe(VI) as expressed in the form of the species FeO_4^{2-} , such as from the salt K_2FeO_4 is unstable in neutral aqueous solutions and decomposes according to the following equation:



It is an object of the present invention to provide a novel method for electrochemical preparation of Fe(VI) salts which overcomes the unattractive features of anodic dissolution synthesis, and is therefore capable of producing concentrated Fe(VI), while also avoiding Fe(VI) decomposition losses during synthesis, and without the need for precipitating agents.

BRIEF DESCRIPTION OF THE INVENTION

The invention relates to an electrochemical process to prepare solid Fe(VI) salts, by an electrolytic cell comprising two half-cells which are in an electrochemical contact with one another through an electrically neutral ionic conductor, wherein one of said half-cells comprises a cathode and the other half-cell comprises at least 1% by weight of an iron containing material in the solid form, wherein a power supply is used to oxidize the iron containing material to a solid Fe(VI) salt. Material additions to the iron containing material, and to the electrically neutral ionic conductor can change the characteristics of the prepared solid Fe(VI) salt.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1: is a diagrammatic illustration of an electrolytic process for preparing solid Fe(VI) salts.

DETAILED DESCRIPTION OF THE INVENTION

The novel battery according to the present invention is based on Fe(VI) (hereafter also called "super iron") half cell in contact with a cathode half cell through an electrically neutral ionic conductor. The preparation of this solid super iron salt is

based on the electrolytic oxidation of a half-cell containing at least 1% by weight of iron in its 0 (metal or Fe(0)), and/or +2 (Fe(II)), and/or +3 (Fe(III)) valence state. The electrically neutral ionic conductor has a Fe(VI) salt dissolving capacity less than the quantity of prepared Fe(VI) salt. This undissolved prepared Fe(VI) salt remains in the solid phase. This overcomes the unattractive features of anodic dissolution synthesis, and is capable of producing more concentrated Fe(VI), which avoids solution phase Fe(VI) decomposition losses during synthesis, and which is formed without the need for precipitating agents.

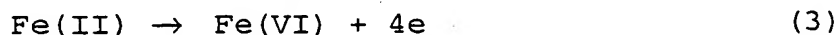
The solid Fe(VI) salt is illustrated by $MFeO_4$, M being an alkali earth cation. Other typical examples includes a cation, selected from the alkali cations, in the form M_2FeO_4 , or from the group consisting of the transition metal cations, or containing, cations of group III, group IV and group V elements, with charge +z, and of the form $M_{2/z}FeO_4$. Similarly Fe(VI) salts in addition to oxygen, can contain hydroxide and/or other anions, X, of charge -y, and of the generalized form: $M_{2/z}FeX_{8/y}$. The anion, X, include, but are not limited to: hydroxides, acetates, acetylsalicylates, aluminates, aluminum hydrides, amides, antimonides, arsenates, azides, benzoates, borates,

bromides, bromates, carbides, carbonates, chlorates, perchlorates, chlorides, hypochlorites, chlorites, dithiones, chloroplatinates, chromates, citrates, fluorides, fluosilicates, fluosulfonates, formates, gallium hydrides, gallium nitrides, germanates, hydrides, iodates, iodides, periodate, laurates, manganates, malonates, permanganates, molybdates, myristates,

nitrates, nitrides, nitrites, oxalates, oxides, palmitates, phosphates, salicylates, selenates, selenides, silicates, silicides, stearates, succinates, sulfates, sulfides, sulfites, tartrates, thiocyanates, thionates, tungstates, halides, or chalcogenides. Additionally, each Fe(VI) salts can contain n water or other solvent molecules, W of the generalized form, not limited to: $M_{2/z}FeX_{8/y} \cdot W_n$.

Examples thereof include, but are not limited to, K_2FeO_4 , Na_2FeO_4 , Li_2FeO_4 , Cs_2FeO_4 , Rb_2FeO_4 , H_2FeO_4 , $(NH_4)_2FeO_4$, $BeFeO_4$, $MgFeO_4$, $CaFeO_4$, $SrFeO_4$, $BaFeO_4$, $BaFeO_4 \cdot H_2O$, $BaFeO_4 \cdot 2H_2O$, Hg_2FeO_4 , $HgFeO_4$, Cu_2FeO_4 , $CuFeO_4$, $ZnFeO_4$, Ag_2FeO_4 , $FeFeO_4$, $Fe_2(FeO_4)_3$, $MnFeO_4$, $NiFeO_4$, $CoFeO_4$, $Al_2(FeO_4)_3$, $In_2(FeO_4)_3$, $Ga_2(FeO_4)_3$, $SnFeO_4$, $PbFeO_4$, $Sn(FeO_4)_2$, $Pb(FeO_4)_2$.

Without being bound to any theory, the electrolytic oxidation of iron in its 0 (Fe(0)), +2 (Fe(II)) or +3 (Fe(III)) valence state, requires per iron a minimum electrolysis charge (current x time) sufficient to release 6, 4, or 3 electrons, respectively, in accord with:



Generally the electrolysis charge time depends on the desired final FeO_4^{2-} concentration.

The $\text{Fe}(0)$ in the half-cell is iron metal, in a typical embodiment of high surface area which includes iron powder, iron wire, iron screen or roughened iron surfaces or in another

typical embodiment sheet or solid iron. The $\text{Fe}(\text{II})$ or $\text{Fe}(\text{III})$ in the half-cell is an iron salt in the solid or dissolved state. The $\text{Fe}(\text{II})$ salt includes, but is not limited to FeO , $\text{Fe}(\text{OH})_2$, and salts of the general form $\text{M}_z\text{Fe}(\text{II})\text{X}_y\cdot\text{W}_n$. which contains z or one or more cations, M , and y of one or more cations X , and n of one or more solvent molecules W . The $\text{Fe}(\text{III})$ salt includes, but is not limited to Fe_2O_3 , FeOOH , $\text{Fe}(\text{OH})_3$, and salts of the general form $\text{M}_z\text{Fe}(\text{III})\text{X}_y\cdot\text{W}_n$. which contains z or one or more cations, M , and y of one or more cations X , and n of one or more solvent molecules W .

The iron ($\text{Fe}(0)$, $\text{Fe}(\text{II})$ or $\text{Fe}(\text{III})$) which is to be oxidized is placed in contact with a conductive material, such as graphite, carbon black or a metal. These and other agents can be formed by mixing with the iron as a powder, and the powder can be pressed with these and other agents to improve mechanical strength. Rather than mixing with a conductive material, the iron salt can be placed in direct contact with a conductive material. These conductive materials include, but are not limited to a planar conductive surface, a wire, a porous conductive substrate or a conductive grid.

The cathode of the battery may be selected from the known list of materials capable of being reduced, typical examples

being metal and non-metal inorganic salts, and organic compounds including aromatic and non-aromatic compounds.

The electrically neutral ionic conductor utilized in the battery according to the present invention, comprises a medium that can support current density during battery discharge. Typical representative ionic conductor is an aqueous solutions preferably containing a high concentration of a hydroxide such as KOH.

In typical embodiments, the electrically neutral ionic conductor comprises common ionic conductor materials used in electrolytic processes which include, but are not limited to an aqueous solution, a non-aqueous solution, a conductive polymer, a solid ionic conductor and a molten salt.

According to another embodiment, the invention provides means to impede transfer of chemically reactive species, or prevent electric contact between the anode and Fe(VI) salt cathode. Said means includes, but is not limited to a membrane a ceramic frit, or agar solution, positioned to separate said half cells or a non-conductive separator configured with open channels, grids or pores.

A material addition, from 0.1 to 50%, and in the preferred range from 1 to 10%, to the electrically neutral ionic conductor, or to the iron in its 0, +2 or +3 valence state, can modify the quantity and the physical, chemical and electrochemical characteristics of the Fe(VI) salt which will be formed, and or modify the voltage and coulombic efficiency of the Fe(VI) electrolytic formation process. A material addition of a barium compound, can be used to decrease the solubility of

Fe(VI) salts to improve the quantity of Fe(VI) salt produced. Barium additions include, but are not limited to, barium(II) compounds, as illustrated by BaX_2 and BaY_3 , where X and Y are anions as previously described.

A material addition of an oxygen containing compound, be used to increase quantity of Fe(VI) salt produced. Oxygen containing compounds include, but are not limited to, hydroxide compounds, such as MOH compounds, M being an alkali cation. Another typical example of hydroxides salts contain alkali earth, M' cations, other typical examples includes a cation, selected from the group consisting of the transition metal cations, or containing, cations of group III, group IV and group V elements. Another typical example of oxygen containing compounds includes oxides containing alkali, alkali earth, M' cations, or a cation, selected from the group consisting of the transition metal cations, or containing, cations of group III, group IV and group V elements.

A material addition of a manganese compound, can be used. Manganese additions include, but are not limited to, manganese(IV) compounds, as illustrated by MnO_2 , $\text{Mn}(\text{OH})_4$, MnO_2 , or MnS_2 , manganese(III) salts, as illustrated by Mn_2O_3 , and $\text{Mn}(\text{OH})_3$, and Mn(II) salts, as illustrated by MnO , and $\text{Mn}(\text{OH})_2$. Other typical manganese additions are manganese(VII) compounds illustrated by a permanganate salt MMnO_4 , or Mn_2O_7 , or manganese(VI) compounds illustrated by manganate salt, M_2MnO_2 , M being an alkali cation. Another typical example of manganate and permanganate salts contain alkali earth, M' cations, other typical examples includes a cation, selected from the group

consisting of the transition metal cations, or containing, cations of group III, group IV and group V elements.

A material addition of a cobalt compound can be used. Cobalt additions include, but are not limited to, cobalt(III) compounds, as illustrated by Co_2Y_3 , or CoX_3 , Y being oxygen or in other typical examples being a chalcogenide, chromate, molybdate, silicate, malonate, succinate, tartrate, selenate, sulfate, or sulfite anions. X being a hydroxide anion, or in other typical examples, X being a halide anion, nitrate, bromate, chlorate, perchlorate, acetate, oxalate, carbonate, benzoate, hypochlorite, chlorite, dithionate, formate, iodate, or periodate anions. Other typical cobalt additions are Co(II) compounds such as CoY , CoX_2 and Co(IV) compounds such as and CoY_2 , and CoX_4 .

A material addition of lithium containing compound, can be used. Lithium containing compounds include, but are not limited to lithium: hydroxides, carbonates, acetates, acetylsalicylates, aluminates, aluminum hydrides, amides, antimonides, arsenates, azides, benzoates, borates, bromides, carbides, chlorates, perchlorates, chlorides, chloroplatinates, chromates, citrates, fluorides, fluosilicates, fluosulfonates, formates, gallium hydrides, gallium nitrides, germanates, hydrides, iodates, iodides, laurates, manganates, permanganates, molybdates, myristates, nitrates, nitrides, nitrites, oxalates, oxides, palmitates, phosphates, salicylates, selenides, silicates, silicides, stearates, sulfates, sulfides, sulfites, tartrates, thiocyanates, thionates, tungstates.

A material addition of various salts can be used to alter the required electrolysis voltage and/or alter the characteristics of the produced Fe(VI) salt. These compounds include indium compounds, which can lower the required electrolysis voltage, tin compounds, such as SnO, and SnO₂, tungsten compounds, such as WO₃, and WO₂, and cobalt compounds, such as CoO and Co₂O₃. Indium additions include, but are not limited to, indium(III) compounds, as illustrated by In₂Y₃, or InX₃, where X and Y are previously described. Other typical indium additions are In(II) compounds as InY, InX₂ and In(IV) compounds such as InY₂, and InX₄.

DETAILED DESCRIPTION OF FIGURE 1

Figure 1 illustrates schematically an electrochemical cell (10) based on an Fe(0), Fe(II) or Fe(III) half cell, an electrically neutral ionic conductor and an cathode. The cell contains an

electrically neutral ionic conductor (22), such as a concentrated aqueous solution of KOH or Ba(OH)₂ in contact with an Fe(0), Fe(II) or Fe(III) anode (14), typically a solid Fe(III) salt as a pressed pellet containing graphite powder and solid K₂FeO₄. Oxidation of Fe(0), Fe(II) or Fe(III) ions is achieved via electrons removed by the power supply (14) to form the solid Fe(VI) salt. The cathode electrode 12, receives this electrons, such as in the form of a metal salt, is also in contact with the electrically neutral ionic conductor (22). Electrons are released in the oxidation of the anode. Optionally, the cell may contain an ion selective membrane (20) as a separator, for minimizing the non-electrochemical interaction between the cathode and the anode.

The invention will be hereafter illustrated by the following Examples, being understood that the Examples are presented only for a better understanding of the invention without implying any limitation thereto, the invention being covered by the appended Claims.

EXAMPLE 1

An experiment was carried out, the object being to determine electrically neutral ionic conductors which have a limited Fe(VI) salt dissolving capacity, and which are thereby in a cell are compatible to produce solid Fe(VI) salt. For a cell containing a volume, V , of solution, the maximum dissolving

capacity is $V \times S$. S is the maximum solubility of the Fe(VI) salt in various electrically neutral ionic conductors. A lower value of S will increase the fraction of produced Fe(VI) which is in the solid state. A very low value of S will determine that the significant majority of produced Fe(VI) salt is in the solid state. A variety of solutions can be used as electrically ionic conductors. Table 1 presents the measured solubility two examples of Fe(VI) salts, BaFeO_4 and K_2FeO_4 , in a variety of solutions. As seen in Table 1, each of these solutions has a limited solubility of Fe(VI) salt and can be used in to produce solid Fe(VI) salt when it is formed in a quantity greater than the limited dissolving capacity.

Table 1. Examples of the dissolving capacity of various aqueous and non-aqueous solutions for Fe(VI) salts, as expressed by the solution solubility; where for a cell containing a volume, V, of solution, the dissolving capacity is V x the Solubility.

Solution	Salt	S. Solubility
water	BaFeO ₄	<< 10 ⁻⁵ M
aqueous 0.2 M Ba(OH) ₂	BaFeO ₄	<< 10 ⁻⁵ M
aq. 5 M KOH & satd Ba(OH) ₂	BaFeO ₄	< 2x10 ⁻⁴ M
aq. 5 M KOH & satd Ba(OH) ₂	K ₂ FeO ₄	< 2x10 ⁻⁴ M
aq. 5 M KOH	BaFeO ₄	5x10 ⁻⁴ M
aq. 5 M KOH	K ₂ FeO ₄ + Ba(OH) ₂	5x10 ⁻⁴ M
aq. 5 M KOH	K ₂ FeO ₄	7x10 ⁻² M
aq. 5 M LiOH	K ₂ FeO ₄	9x10 ⁻¹ M
aq. 5 M NaOH	K ₂ FeO ₄	1.4 M
aq. 5 M CsOH	K ₂ FeO ₄	3.5x10 ⁻² M
aq. 10 M NaOH	K ₂ FeO ₄	5x10 ⁻¹ M
aq. 10 M KOH	K ₂ FeO ₄	1x10 ⁻² M
aq. satd. KOH	K ₂ FeO ₄	2x10 ⁻³ M
acetonitrile	BaFeO ₄ , K ₂ FeO ₄	<< 10 ⁻⁵ M
acetone	BaFeO ₄ , K ₂ FeO ₄	<< 10 ⁻⁵ M
hexane	BaFeO ₄ , K ₂ FeO ₄	<< 10 ⁻⁵ M
chloroform	BaFeO ₄ , K ₂ FeO ₄	<< 10 ⁻⁵ M
sulfonane	BaFeO ₄ , K ₂ FeO ₄	<< 10 ⁻⁵ M
1,4 - dioxane	BaFeO ₄ , K ₂ FeO ₄	<< 10 ⁻⁵ M
acetonitrile + 1 M LiClO ₄	BaFeO ₄ , K ₂ FeO ₄	<< 10 ⁻⁵ M
ethylene carbonate (EC)	BaFeO ₄ , K ₂ FeO ₄	<< 10 ⁻⁵ M
γ-butyrolactone (BLA)	BaFeO ₄ , K ₂ FeO ₄	<< 10 ⁻⁵ M
tetrahydrofuran (THF)	BaFeO ₄ , K ₂ FeO ₄	<< 10 ⁻⁵ M
Dimehtoxyethane (DME)	BaFeO ₄ , K ₂ FeO ₄	<< 10 ⁻⁵ M
EC + 0.5 M LiClO ₄	BaFeO ₄ , K ₂ FeO ₄	<< 10 ⁻⁵ M
BLA + 0.5 M LiClO ₄	BaFeO ₄ , K ₂ FeO ₄	<< 10 ⁻⁵ M
THF + 1 M LiClO ₄	BaFeO ₄ , K ₂ FeO ₄	<< 10 ⁻⁵ M
DME + 1 M LiClO ₄	BaFeO ₄ , K ₂ FeO ₄	<< 10 ⁻⁵ M

Example 2

An experiment was carried out, the object being to produce electrolytic solid Fe(VI) salt using an electrochemical cell as diagramtically illustrated in Fig. 1. The electrochemical cell configuration consisted of a 2 cm diameter button cell comprised of an upper (cathode) section, pressing onto a mid (separator) section, pressing onto a lower (anode) section.

The upper section of the electrochemical cell configuration comprises an upper inverted metal dish plate (the cathode cap) pressing onto a metal washer type spring, which presses onto a metal screen (the cathode collector), pressing onto a metal hydride material removed from a discharge commercial metal hydride battery. The quantity of metal hydride is determined to be in coulombic excess of the iron material, as determined in accord with equations 2, 3 and 4. The mid section consists of a separator material removed from a commercial metal hydride battery and is surrounded by a PTFE washer to prevent direct contact or electrical shorting of the upper and lower section. Various electrolytes as electrically neutral ionic conductors, in various amounts, were tested, and are added to the separator and anode material. The lower section consists of a pressed mixed powder pressed into a bottom metal dish plate. Various cells were formed with powders containing a variety of iron materials in the Fe(0), Fe(II), or Fe(III) valence state, as well as various tested additives and added conductors.

An oxidizing current to was applied to the anode using a constant current power supply connected for a fixed time to the upper and lower plates of the electrochemical cell configuration

A variety of currents and times were examined in various cells. Each cell was then open, and the solid iron material was removed. The percentage of the original iron containing material that was converted to solid Fe(VI) salt was determined by the chromite method to probe the iron valence state, determined by Fe(VI) redissolution as FeO_4^{2-} , and oxidation of

chromite, according to (where chromate generated is titrated with a standard ferrous ammonium sulfate solution, using a sodium diphenylamine sulfonate indicator):

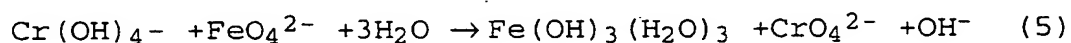
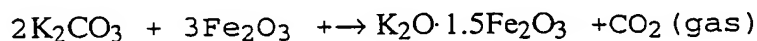


Table 2 summarizes the percentage of Fe(VI) salt that was produced from the original iron containing material for a variety of formed electrolytic cells. As can be seen in the Table, various solid Fe(VI) salts can be directly formed by this procedure, and this procedure varies with added conductor, additives, electrolyte and electrolysis time and current. These cells are provided only by way of example, and are not limiting. It is evident that further variation of the many cell parameters including, but not limited to particle size of the pressed powders, anode, separator and cathode thicknesses and other electrolysis conditions can be used to further increase the efficiency, percentage and type of produced the produced(VI) solid salt.

Table 2. In each case 25 mAh of the iron material, as determined by equation 2, 3 or 4 is used. In the anode powder, the molar ratio of any additive is indicated, as well the percent by weight of the conductor. K=KOH, Ba=Ba(OH)₂; BaO=BaO; CB = carbon black, Fe(0) = iron metal powder; I = K₂O·1.5Fe₂O₃; and II = BaO·1.5Fe₂O₃ are produced from a stoichiometric mixture

of a carbonate salt and ferric oxide, pressing the mixture at 3000 kg, and heating in air at 900°C for 24 hours produced according to:



Iron Type	Additive/Ratio	Conductor/%	Electrolyte (x mg/y molar)	Charging current, time	% Fe(VI) salt produced
Fe(0)	Ba/(1:1)	CB/40%	54 /13.5 K & 6/satd B	2 mA, 30 hr	21.2%
Fe(OH) ₂	Ba/(1:1)	CB/40%	54 /13.5 K & 6/satd B	2 mA, 30 hr	12.2%
Fe ₂ O ₃	Ba/(1:1)	CB/40%	54 /13.5 K & 6/satd B	2 mA, 30 hr	14.3%
Fe(OH) ₃	Ba/(1:1)	CB/40%	54 /13.5 K & 6/satd B	2 mA, 30 hr	18.6%
I	K/(1:1)	CB/30%	50/12 KOH	3 mA, 20 hr	2.2%
II	Ba/(1:2)	CB/40%	60 /13.5 K & satd B	2 mA, 30 hr	69.1%
II	BaO(1:2)	CB/40%	60 /13.5 K & satd B	2 mA, 30 hr	56.8%
II	BaO(1:2)&10%CsOH	CB/40%	60 /13.5 K & satd B	2 mA, 30 hr	65.6%
II	BaO(1:2)	CB/60%	60 /13.5 K	2 mA, 30 hr	50.7%
II	BaO(1:2)	CB/20%	60 /12 K	2 mA, 30 hr	35.3%
II	BaO(1:2)	CB/30%	60 /12 K	2 mA, 30 hr	52.8%
II	BaO(1:1)	graphite/30%	50 /12 K	2 mA, 30 hr	12.7%
II	none	graphite/30%	50 /satd B	2 mA, 30 hr	8.4%
II	BaO(1:2)	CB/30%	50 /12 K	2 mA, 60 hr	49.3%
II	BaO(1:2)	CB/30%	50 /12 K	2 mA, 20 hr	44.6%
II	BaO(1:2)	CB/30%	50 /12 K	2 mA, 10 hr	31.0%
II	BaO(1:2)	CB/30%	50 /12 K	2 mA, 5 hr	25.2%
II	BaO(1:2)	CB/30%	50 /12 K	5 mA, 12 hr	20.3%
II	BaO(1:2)	CB/30%	50 /12 K	1 mA, 60 hr	31.9%
II	BaO(1:2)	CB/30%	50 /10 K	2 mA, 30 hr	25.9%
II	BaO(1:2)	CB/30%	50 /8 K	2 mA, 30 hr	12.3%
II	BaO(1:2)	CB/30%	50 /6 K	2 mA, 30 hr	10.6%

CLAIMS:

1. A process for preparing Fe(VI) salts which comprising two half-cells which are in an electrochemical contact with one another through an electrically neutral ionic conductor, wherein ~~one of said half-cells comprises a cathode and the other half-~~
cell comprises at least 1% of weight of an iron containing material, wherein a power supply is used to oxidize the iron containing material to a solid Fe(VI) salt.
2. The process according to Claim 1, wherein said iron containing material is a solid or dissolved Fe(III) salt.
3. The process according to Claim 1, wherein said iron containing material is a solid or dissolved Fe(II) salt.
4. The process according to Claim 1, wherein said iron containing material is iron metal, Fe(0).
5. The process according to Claim 2 or 3, wherein said salt is an oxide or a hydroxide or contains the anions, selected from the group consisting of acetates, acetylsalicylates, aluminates, aluminum hydrides, amides, antimonides, arsenates, azides, benzoates, borates, bromides, bromates, carbides, carbonates, chlorates, perchlorates, chlorides, hypochlorites, chlorites, dithionate, chloroplatinates, chromates, citrates, fluorides, fluosilicates, fluosulfonates, formates, gallium hydrides, gallium nitrides, germanates, hydrides, iodates, iodides, periodate, laurates, manganates, malonates, permanganates, molybdates, myristates, nitrates, nitrides, nitrites, oxalates, palmitates, phosphates, salicylates, selenates, selenides, silicates, silicides, stearates,

succinates, sulfates, sulfides, sulfites, tartrates, thiocyanates, thionates, tungstates, halides, or chalcogenides.

6. The process according to Claim 2 or 3, wherein said salt includes a cation, selected from the group consisting of the alkali cations, H^+ , the alkali earth cations, transition metal cations, or containing cations of group III, group IV and group

V or ammonium or organic ammonium cations.

7. The process according to Claims 1 to 4, wherein said electrically neutral ionic conductor is an aqueous solution.

8. The process according to Claims 1 to 4, wherein said electrically neutral ionic conductor is a nonaqueous solution.

9. The process according to Claims 1 to 4, wherein said electrically neutral ionic conductor is a conductive polymer.

10. The process according to Claims 1 or 2, wherein said electrically neutral ionic conductor is a solid ionic conductor.

11. The process according to Claims 1 to 4, wherein said electrically neutral ionic conductor is a molten salt.

12. The process according to Claims 7 to 11, wherein said neutral ionic conductor contains a dissolved salt.

13. The process according to Claims 7 to 9, wherein said neutral ionic conductor contains a dissolved liquid.

14. The process according to Claim 13, wherein said dissolved liquid is an organic solvent.

15. The process according to Claims 7-11, wherein said neutral ionic conductor contains the concentration of up to saturation in hydroxide ions.

16. The process according to Claim 12, wherein said dissolved salt is an iron salt in a concentration of up to saturation.

17. The process according to Claim 16, wherein said iron salt an Fe(VI) salt.

18. The process according to Claim 16, wherein said iron salt an Fe(III) salt.

19. The process according to Claim 16, wherein said iron salt an Fe(II) salt.

20. The process according to Claim 12, wherein said dissolved salt is an oxide or a hydroxide or contains the anions, selected from the group consisting of acetates, acetylsalicylates, aluminates, aluminum hydrides, amides, antimonides, arsenates, azides, benzoates, borates, bromides, bromates, carbides, carbonates, chlorates, perchlorates, chlorides, hypochlorites, chlorites, dithionate, chloroplatinates, chromates, citrates, fluorides, fluosilicates, fluosulfonates, formates, gallium hydrides, gallium nitrides, germanates, hydrides, iodates, iodides, periodate, laurates, manganates, malonates, permanganates, molybdates, myristates, nitrates, nitrides, nitrites, oxalates, palmitates, phosphates, salicylates, selenates, selenides, silicates, silicides, stearates, succinates, sulfates, sulfides, sulfites, tartrates, thiocyanates, thionates, tungstates, halides, or chalcogenides.

21. The process according to Claim 12, wherein said dissolved salt includes a cation, selected from the group consisting of the alkali cations, H^+ , the alkali earth cations, transition metal cations, or containing cations of group III, group IV and group V or ammonium or organic ammonium cations.

22. The process according to Claims 1 to 4, further characterized in that said iron containing material is in contact with a conductive material.

23. The process according to Claim 22, wherein said conductive material is selected from graphite, carbon black and a metal.

24. The process according to Claim 22, wherein said iron containing material-conductive material comprises a mixed pressed powder.

25. The process according to Claim 22, wherein said iron containing material-conductive material comprises a planar surface or a wire.

26. The process according to Claim 22, wherein said iron containing material-conductive material comprises a porous substrate or grid.

27. The process according to Claims 1 to 4 further comprising means to impede transfer of chemically reactive species between said anode and said other half cell.

28. The process according to Claim 27, wherein said means is a non conductive separator configured with open channels, grids or pores.

29. The process according to Claim 26 in which said means to impede transfer of chemically reactive species comprises a membrane positioned to separate said half cells.

30. The process according to Claim 1, wherein said cathode includes a non metal inorganic salt capable of being reduced.

31. The process according to Claim 1, wherein said cathode includes a metal inorganic salt capable of being reduced.

32. The process according to Claim 1, wherein said cathode includes an organic compound capable of being reduced.

33. The process according to Claim 32, wherein said organic compound is selected from the group consisting of aromatic and non-aromatic compounds.

~~34. The process according to Claims 1, further characterized in~~
that said neutral ionic conductor contains an added enhancing material to modify the Fe(VI) salt production.

35. The process according to Claims 1 to 4, further characterized in that said iron containing material contains an added enhancing material to modify the Fe(VI) salt production.

36. The process according to Claim 34 or 35, wherein said enhancing material is a Ba(II) compounds.

37. The process according to Claim 34 or 35, wherein said enhancing material is an oxygen containing compound, such as an oxide or hydroxide compound.

38. The process according to Claim 34 or 35, wherein said enhancing material is an indium containing compound.

39. The battery according to Claim 1, wherein said enhancing material is a manganese containing compound.

40. The process according to Claim 10, wherein said charging voltage altering material, is a lithium containing compound.

41. The process according to Claim 34 or 35, wherein said enhancing material is a tin containing compound.

42. The process according to Claim 34 or 35, wherein said enhancing material is a tungsten containing compound.

43. The process according to Claim 10, wherein said enhancing material is a cobalt containing compound.

44. The process according to Claim 1, wherein said cathode includes an oxide or a hydroxide or contains the anions, selected from the group consisting of chalcogenide, chromate, molybdate, silicate, malonate, succinate, tartrate, selenate, sulfate, sulfite, halide, nitrate, bromate, chlorate, perchlorate, acetate, oxalate, carbonate, benzoate, hypochlorite, chlorite, dithionate, formate, iodate, periodate, carbonates, acetates, acetylsalicylates, aluminates, aluminum hydrides, amides, antimonides, arsenates, azides, benzoates, borates, bromides, carbides, chlorates, chlorides, chloroplatinates, chromates, citrates, fluorides, fluosilicates, fluosulfonates, gallium hydrides, gallium nitrides, germanates, hydrides, iodides, laurates, manganates, permanganates, molybdates, myristates, nitrates, nitrides, nitrites, oxalates, palmitates, phosphates, salicylates, selenides, silicates, silicides, stearates, sulfates, sulfides, sulfites, tartrates, thiocyanates, thionates, or tungstates.

45. The process according to Claim 1, wherein said cathode includes a cation, selected from the group consisting of the alkali cations, H^+ , the alkali earth cations, transition metal cations, or containing cations of group III, group IV and group V or ammonium or organic ammonium cations.

46. The process substantially as described in the specifications and in any one of Claims 1 to 45.

For the Applicant

Simon Lave

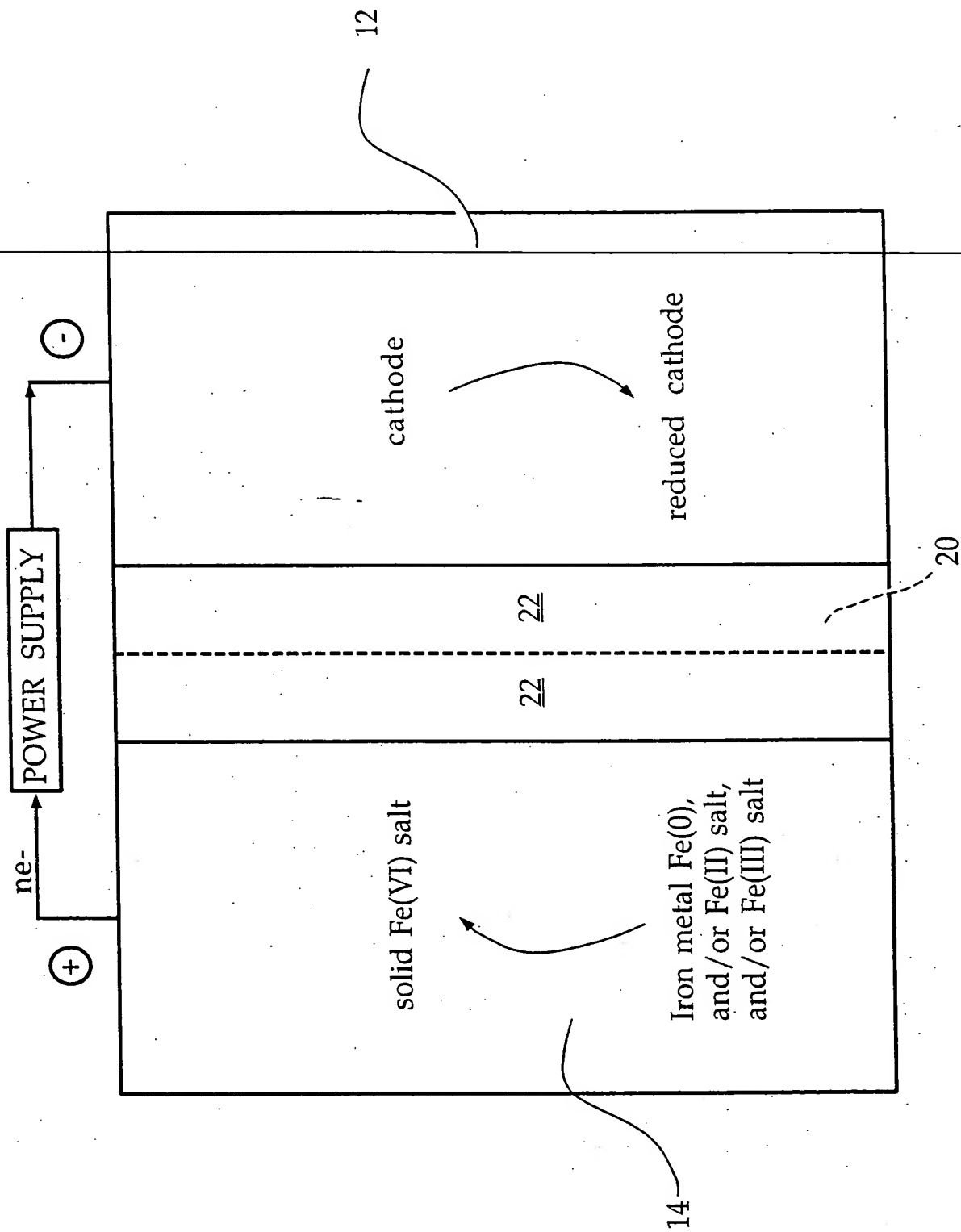


FIG. 1